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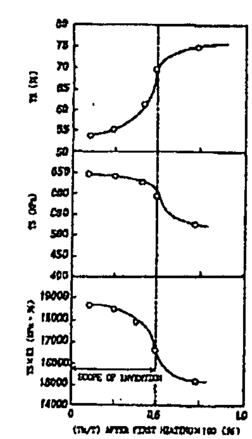
(54) **HIGH STRENGTH THIN STEEL SHEET, HIGH STRENGTH ALLOYED HOT-DIP ZINC-COATED STEEL SHEET, AND METHOD FOR PRODUCING THEM**

(57) The present invention provides a high strength thin excellent workability and galvanizability, having a composition comprising from 0.01 to 0.20 wt.% C, up to 1.0 wt.% Si, from 1.0 to 3.0 wt.% Mn, up to 0.10 wt.% P, up to 0.05 wt.% S, up to 0.10 wt.% Al, up to 0.010 wt.% N, up to 1.0 wt.% Cr, from 0.001 to 1.00 wt.% Mo, and the balance Fe and incidental impurities, wherein a band structure comprising a secondary phase has a thickness satisfying the relation $T_b / T \leq 0.005$ (where, T_b: average thickness of the band structure in the thickness direction of steel sheet; T: steel sheet thickness), and a manufacturing method thereof, and a manufacturing method of a high strength hot-dip galvanized steel sheet or a high strength galvannealed steel sheet applying hot-dip galvanizing or further galvannealing, and giving an excellent workability, a high tensile strength, and excellent galvanizability, coating adhesion and corrosion resistance.

Fig. 1



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Descripti n

Technical Fi ld

[0001] The present invention relates to a high strength thin steel sheet (substrate for galvanizing) suitable for such uses as an automobile body and a high strength galvannealed steel sheet made from the high strength thin steel sheet, as well as manufacturing methods of the high strength thin steel sheet, the high strength hot-dip galvanized steel sheet and the high strength galvannealed steel sheet.

Background Art

[0002] From the point of view of achieving a high safety, a smaller weight, a lower fuel/cost ratio, and hence cleaner earth environments, there are increasing applications of high strength steel sheets and high strength hot-dip galvanized steel sheets excellent in corrosion resistance as steel sheets for automobiles.

[0003] In order to manufacture high strength hot-dip galvanized steel sheets among others, it is necessary to previously manufacture a material sheet having a good galvanizability, and giving desired strength and workability after passing through a hot-dip galvanizing bath, and after application of a galvannealing treatment.

[0004] In order to increase strength of a steel sheet, in general, it is the common practice to add solid solution hardening elements such as P, Mn and Si and precipitation hardening elements such as Ti, Nb and V.

[0005] When a steel sheet containing these elements added as described above is treated on a continuous hot-dip galvanizing line (CGL), the steel sheet is subjected to annealing at a temperature of over the Ac1 transformation point, and further, a low cooling rate makes it difficult to obtain a high tensile strength: achievement of a high tensile strength requires addition of alloy elements in large quantities, and this leads to a higher cost.

[0006] Addition of alloy elements in large quantities is known to cause serious deterioration of galvanizing property. The quantities of added alloy elements are limited also from the point of view of galvanizability.

[0007] Because of the contradictory actions of alloy elements in the substrate steel sheet on strength and galvanizability, it has been very difficult to manufacture a high strength hot-dip galvanized steel sheet excellent in galvanizability on a continuous hot-dip galvanizing line.

[0008] In the case of high strength steel sheet, it has further been difficult to manufacture a hot-dip galvanized steel sheet excellent in workability because of low properties relating to workability such as elongation.

[0009] As a high strength steel sheet having a high workability, on the other hand, there has conventionally been proposed a composite (containing residual austenite) mainly comprising martensite with ferrite as the base metal.

[0010] This composite structure steel sheet is non-aging at room temperature, has a low yield ratio [: {yield strength (YS) } / { tensile strength (TS) }], and is excellent in workability and hardenability after working.

[0011] A known manufacturing method of a composite structure steel sheet is to heat a steel sheet at a temperature within the (α + γ) region, and then rapid cool the steel sheet by water cooling or gas cooling. It is also known that a higher cooling rate leads to the necessity of a smaller number of necessary alloy elements and a smaller amount of addition.

[0012] However, when a conventional composite structure steel sheet is subjected to hot-dip galvanizing at a temperature of about 500 °C, or further, to a heating-galvannealing treatment, hard martensite, a targeted secondary phase, does not occur, in addition to the primary phase ferrite, but there are generated soft cementite, pearlite and bainite. This results in a decrease in tensile strength and appearance of an upper yield point, leading to an increase in yield point, or further, an yield elongation.

[0013] Temper softening tends to be easily caused according as the quantities of added alloy elements become smaller. Large quantities of these alloy elements causes, on the other hand, a decrease in hot-dip galvanizing property.

[0014] After all, hard martensite is not generated during the galvanizing step even in the composite structure steel sheet, but soft cementite, pearlite and bainite are produced. It has therefore been difficult to achieve compatibility between workability brought about by the primary phase ferrite and a high strength based on the secondary phase martensite, and a satisfactory galvanizability in the conventional art.

[0015] In a galvanized steel sheet, on the other hand, the galvanized steel sheet is required to be excellent in coating adhesion so as to eliminate the necessity to prevent peeling of the galvanizing layer upon press working and maintain a die.

[0016] In order to increase strength of a steel sheet, in general, it is the common practice to add solid solution hardening elements (easily oxidizable elements) such as Mn as described above. These elements however become oxides during reduction-annealing before galvanizing, are concentrated on the steel sheet surface, and reduce wettability by the molten zinc resulting in production of non-galvanized defects on the steel sheet surface in which the galvanizing layer hardly adheres to the steel sheet surface.

[0017] The cause is as follows. A recrystallization annealing atmosphere is a reducing atmosphere for Fe, which

does not allow production of Fe oxides, but is an oxidizing atmosphere for easily oxidized elements such as Mn. These elements are concentrated on the steel sheet surface, form an oxide film, and thus reduce the contact area between the molten zinc and the steel sheet.

[0018] As a manufacturing method of a high strength hot-dip galvanized steel sheet, a method of regulating the cooling rate during annealing upon galvanizing is disclosed in Japanese Unexamined Patent Publication No. 55-50455. The disclosed method contains no description about a method for improving galvanizability. Particularly, when the Mn content in the material steel sheet is over 1%, it is difficult to prevent non-galvanized defects, and the method teaches nothing about a method for improving coating adhesion.

[0019] Under the current actual circumstances, therefore, the high strength steel sheet excellent in workability attraction as a high strength material for automobile lacks actual means to be applied as a surface-treated steel sheet excellent also in coating adhesion, though not excellent in workability, in the form of a hot-dip galvanized steel sheet.

[0020] Japanese Examined Patent Publication No. 7-9055 discloses a method of applying galvanizing to a steel sheet pickled after annealing as a method for improving the galvannealing rate of a P-added steel. This method has however an object to improve the galvannealing rate, not to prevent non-galvanized defects.

[0021] The above-mentioned method teaches nothing about the dew point, the hydrogen concentration and temperature of atmosphere gas upon annealing applied immediately prior to galvanizing. Non-galvanized defects are considered to occur more frequently for certain combinations of the kind of steel and the annealing atmosphere.

[0022] Japanese Unexamined Patent Publication No. 7-268584 discloses a method of conducting secondary annealing at a temperature determined in response to the P content in steel. This is however based on a technical idea that the temperature region for preventing brittleness of a steel sheet is dependent upon the P content in steel, not a disclosure of a temperature for improving galvanizability.

[0023] The present invention has an object to solve the aforementioned problems involved in the conventional art, and to provide a high strength thin steel sheet serving as a substrate for galvanizing which is excellent in workability and strength even after hot-dip galvanizing or further a galvannealing treatment, and gives an excellent galvanizability as well as an excellent corrosion resistance, a galvannealed steel sheet, made of this high strength thin steel sheet excellent in workability, coating adhesion and corrosion resistance, and manufacturing methods thereof.

[0024] More specifically, an object of the present invention is to provide a high strength thin steel sheet excellent in workability which satisfies conditions including a yield ratio of up to 70% and a TS × El value of at Least 16,000 MPa • %, and permits prevention of occurrence of non-galvanized defects, a high strength galvannealed steel sheet made of the above high strength thin steel sheet, excellent in workability, coating adhesion and corrosion resistance, as well as manufacturing methods of such high strength thin steel sheet, high-strength hot-dip galvanized steel sheet and high strength galvannealed steel sheet.

Disclosure of Invention

[0025] As a result of extensive studies carried out to solve these problems, the present inventors obtained the following findings (1) to (4):

(1) Dispersion of band structures in steel sheet

[0026] A thin steel sheet in which a high workability and a high tensile strength are simultaneously achieved, with a satisfactory galvanizability, is available, from the point of view of improving mechanical properties, by using a steel sheet having a prescribed chemical composition and heating the steel sheet to a temperature of at least a prescribed level to cause dispersion of a band structure particularly, comprising a secondary phase (comprising mainly cementite, pearlite and bainite and only partially martensite and residual austenite) to a prescribed extent in the steel sheet.

(2) Two-stage heating-pickling

[0027] A high strength hot-dip galvanized steel sheet, which permits prevention of non-galvanized defects, excellent in workability, coating adhesion and corrosion resistance is obtained, from the point of view of improving galvanizability, by using a steel sheet having a prescribed chemical composition, heating the steel sheet to a temperature of at least a prescribed level in an annealing furnace, then after cooling, removing a concentrated layer of steel constituents on the steel sheet surface, then annealing again the steel sheet at a prescribed heating-reduction temperature in a prescribed reducing atmosphere on a continuous hot-dip galvanizing line, and then, subjecting the steel sheet to hot-dip galvanizing.

[0028] In other words, an important point for ensuring a high galvanizability in the method of reduction-annealing a once annealed steel sheet is the atmosphere used upon reduction-annealing.

[0029] An oxide film poor in wettability with the molten zinc impairs galvanizability of the steel sheet immediately

after annealing unless the atmosphere sufficiently reduces P-based pickling residues produced on the steel sheet surface upon pickling the once annealed steel sheet. In the manufacturing method of a high strength hot-dip galvanized steel sheet of the present invention, the once annealed steel sheet is annealed again at a prescribed heating-reduction temperature in a prescribed reducing atmosphere, and the subjected to hot-dip galvanizing.

(3) One-stage heating

[0030] As a result of further studies, the present inventors obtained the following findings. Satisfactory galvanizability, workability and coating adhesion can be achieved through one-stage heating by subjecting the steel sheet to hot-dip galvanizing after heating the steel sheet at an appropriate heating temperature in an appropriate atmosphere gas.

(4) Galvannealing treatment

[0031] A high strength galvannealed steel sheet excellent both in coating adhesion after galvannealing and corrosion resistance is available by galvannealing the hot-dip galvanized steel sheet obtained in any of (1) to (3) above preferably under conditions satisfying a prescribed galvannealing temperature.

[0032] The following aspects of the invention and preferred embodiments of these aspects of the invention (1) to (39) were completed on the basis of the aforementioned findings (1) to (4).

(1) A high strength thin steel sheet excellent in workability and galvanizability, having a composition comprising: C: from 0.01 to 0.20 wt.%, Si: up to 1.0 wt.%, Mn: from 1.0 to 3.0 wt.%, P: up to 0.10 wt.%, S: up to 0.05 wt.%, Al: up to 0.10 wt.%, N: up to 0.010 wt.%, Cr: up to 1.0 wt.%, Mo: from 0.001 to 1.00 wt.%, and the balance Fe and incidental impurities, wherein a band structure comprising a secondary phase has a thickness satisfying the relation $T_b / T \leq 0.005$ (where, T_b: average thickness of the band structure in the thickness direction of steel sheet; T: steel sheet thickness).

(2) A high strength thin steel sheet excellent in workability and galvanizability according to (1) above, wherein the high strength thin steel sheet further contains one or more selected from the group consisting of from 0.001 to 1.0 wt.% Nb, from 0.001 to 1.0 wt.% Ti, and from 0.001 to 1.0 wt.% V.

(3) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability, wherein the thickness of the band structure comprising a secondary phase is adjusted within a range of $T_b / T \leq 0.005$ (where, T_b: average thickness of the band structure in the thickness direction of steel sheet, and T: steel sheet thickness) by hot-rolling a slab having a composition comprising: C: from 0.01 to 0.20 wt.%, Si: up to 1.0 wt.%, Mn: from 1.0 to 3.0 wt.%, P: up to 0.10 wt.%, S: up to 0.05 wt.%, Al: up to 0.10 wt.%, N: up to 0.010 wt.%, Cr: up to 1.0 wt.%, Mo: from 0.001 to 1.00 wt.%, and the balance Fe and incidental impurities, coiling the hot-rolled steel sheet at a temperature of up to 750°C, and then, after heating the steel sheet to a temperature of at least 750°C, cooling the same.

Hot roll - coil - reheat - cool

(4) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability according to (3) above, wherein the thickness of the band structure comprising a secondary phase is adjusted within a range of $T_b / T \leq 0.005$ (where, T_b: average thickness of the band structure in the thickness direction of steel sheet; and T: steel sheet thickness) by coiling the hot-rolled steel sheet at a temperature of up to 750°C, then cold-rolling the steel sheet, and then, after heating to a temperature of at least 750 °C, cooling the same.

Hot roll - coil - cold roll - rehea[t] cool.

(5) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability according to (3) or (4) above, comprising the step of, after heating the steel sheet to a temperature of at least 750 °C, applying hot-dip galvanizing in the middle of cooling, or, after application of hot-dip galvanizing subjecting the steel sheet to a heating-galvannealing treatment.

Cold roll - ~~cool~~ - ~~reheat~~ reheat - galvanize -

(6) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability according to (3) or (4) above, comprising the steps of adjusting the thickness of the band structure comprising a secondary phase within a range of $T_b / T \leq 0.005$ (where, T_b: average thickness of the band structure in the thickness direction of steel sheet, and T: steel sheet thickness), then after heating the steel sheet to a temperature of at least 750 °C and cooling the same, further heating the same to a temperature within a range of from 700 to 850 °C, and in the middle of subsequent cooling, subjecting the steel sheet to hot-dip galvanizing, or further to a galvannealing treatment after hot-dip galvanizing.

Cold roll - reheat - cool - anneal - hot dip.

(7) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability according to (5) or (6) above, wherein the coating weight of a hot-dip galvanizing layer, as represented by the coating weight per side of the steel sheet is within a range of from 20 to 120 g/m^2.

(8) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability according to any one of (5) to (7) above, wherein the coating weight of a galvannealed steel sheet after prescribed galvannealing heating treatment, as represented by the coating weight per side of the steel sheet is within a range of from

20 to 120 g/m^2.

(9) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability according to any one of (3) to (8) above, wherein the slab further contains one or more selected from the group consisting of up to 1.0 wt.% Nb, up to 1.0 wt.% Ti and up to 1.0 wt.% V.

(10) A manufacturing method of a high strength thin steel sheet excellent in workability and galvanizability according to any one of (3) to (8) above, wherein the slab further contains one or more selected from the group consisting of from 0.001 to 1.0 wt.% Nb, from 0.001 to 1.0 wt.% Ti and from 0.001 to 1.0 wt.% V.

(11) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, heating the steel sheet to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C in an annealing furnace, removing the concentrated layer of steel constituents on the steel sheet surface by pickling the same after cooling, then, conducting heating-reduction under reducing conditions of P-based oxides remaining as pickling residues on the steel sheet surface, and subjecting the steel sheet to hot-dip galvanizing.

Hot roll - pickle - reheat - pic - anneal - hz

(12) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750 °C, pickling the same, then, after cold-rolling the same, heating the steel sheet to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C in an annealing furnace, cooling the same, removing the concentrated layer of steel constituents on the steel sheet surface by pickling the same, then, conducting heating-reduction under reducing conditions of P-based oxides remaining as pickling residues on the steel sheet surface, and subjecting the steel sheet to hot-dip galvanizing.

(13) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, then heating the steel sheet to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C in an annealing furnace, cooling the same, removing the concentrated layer of steel constituents on the steel sheet surface though pickling, then after heating-reducing the steel sheet under conditions including a dew point of an atmosphere gas within a range of from - 50°C to 0°C and a hydrogen concentration of the atmosphere gas within a range of from 1 to 100 vol.%, subjecting the steel sheet to hot-dip galvanizing.

(14) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, then cold-rolling the steel sheet, heating the same to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C in an annealing furnace, then after cooling the same, removing the concentrated layer of steel constituents on the steel sheet surface though pickling, heating-reducing the steel sheet under conditions including a dew point of an atmosphere gas within a range of from - 50°C to 0°C and a hydrogen concentration in the atmosphere gas within a range of from 1 to 100 vol.%, and then, subjecting the steel sheet to hot-dip galvanizing.

hot roll - coil - pickle - cold r anneal - repick - anneal - hd

(15) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750 °C, pickling the same, then heating the steel sheet to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C in an annealing furnace, then after cooling the same, removing the concentrated layer of steel constituents on the steel sheet surface through pickling, then heating-reducing the steel sheet under conditions in which the heating-reduction temperature: t_1 (°C) satisfies the following equation (1) relative to the P content in steel: P (wt.%), and then subjecting the steel sheet to hot-dip galvanizing:

$$0.9 \le \{[P(wt.\%)+(2/3)] \times 1100\} / \{t_1\ (°C)\} \le 1.1 \qquad (1)$$

(16) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, then cold-rolling the steel sheet, heating the same to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C. or more preferably, from 800°C to 1,000°C in an annealing furnace, then after cooling the same, removing the concentrated layer of steel constituents on the steel sheet surface through pickling, then heating-reducing the steel sheet under conditions in which the heating-reduction temperature: t_1 (°C) satisfies the following equation (1) relative to the P content in steel: P (wt.%), and then subjecting the steel sheet to hot-dip galvanizing:

$$0.9 \le \{[P(wt.\%)+(2/3)] \times 1100\} / \{t_1\ (°C)\} \le 1.1 \qquad (1)$$

(17) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, then heating the steel sheet to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C in a annealing furnace, then after cooling the same, removing the concentrated layer of steel constituents on the steel sheet surface through pickling, then heating-reducing the steel sheet under conditions in which a dew point of the atmosphere gas within a range of from - 50 °C to 0 °C, a hydrogen concentration in the atmosphere gas within a range of from 1 to 100 vol.% and the heating-reduction temperature:t_1 (°C) satisfying the following equation (1) relative to the P content in steel: P (wt.%), and subjecting the steel sheet to hot-dip galvanizing:

$$0.9 \leq \{[P(wt.\%)+(2/3)] \times 1100\} / \{t_1\ (°C)\} \leq 1.1 \qquad (1)$$

(18) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, then cold-rolling the steel sheet, heating the same to a temperature of at least 750°C, or preferably, within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C in an annealing furnace, then after cooling the same, removing the concentrated layer of steel constituents on the steel sheet surface through pickling, then heating-reducing the steel sheet under conditions in which a dew point of the atmosphere gas within a range of from - 50°C to 0°C, a hydrogen concentration in the atmosphere gas within a range of from 1 to 100 vol.% and the heating-reduction temperature: t_1 (°C) satisfying the following equation (1) relative to the P content in steel: P (wt.%), and subjecting the steel sheet to hot-dip galvanizing:

$$0.9 \leq \{[P(wt.\%)+(2/3)] \times 1100\} / \{t_1\ (°C)\} \leq 1.1 \qquad (1)$$

(19) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to any one of (11) to (18) above, comprising the steps of heating the steel sheet at a temperature of at least 750°C, preferably within a range of from 750°C to 1,000°C, or more preferably, from 800°C to 1,000°C, then after cooling the same, applying thereto a pickling method comprising the step of pickling the steel sheet in a pickling liquid having a pH ≤ 1, and a liquid temperature with a range of from 40 to 90°C for a period within a range of from 1 to 20 seconds.

(20) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to any one of (11) to (19) above, comprising the step of heating the steel sheet to a temperature of at least 750°C, or preferably within a range of from 750°C to 1,000 °C, or more preferably, from 800°C to 1,000 °C in an annealing furnace, wherein the pickling liquid after cooling is a hydro chloric acid solution having an HCl concentration within a range of from 1 to 10 wt.%.

(21) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, then heating the same at a heating temperature: T within a range of from 750°C to 1,000°C and satisfying the following equation (2) in an atmosphere gas having a dew point: t of an atmosphere gas satisfying the following equation (3) and a hydrogen concentration within a range of from 1 to 100 vol.%, and then subjecting the steel sheet to hot-dip galvanizing:

$$0.85 \leq \{[P(wt.\%) + (2/3)] \times 1150\} / \{T\ (°C)\} \leq 1.15 \qquad (2)$$

$$0.35 \leq \{[P(wt.\%) + (2/3)] \times (-30)\} / \{t\ (°C)\} \leq 1.8 \qquad (3)$$

(22) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (3) above, comprising the steps of, after coiling the steel sheet at a temperature of up to 750°C, pickling the same, then cold-rolling the same, then heating the same at a heating temperature: T within a range of from 750°C to 1,000°C and satisfying equation (2) in an atmosphere gas having a dew point: t of an atmosphere gas satisfying the following equation (3) and a hydrogen concentration within a range of from 1 to 100 vol.%, and then subjecting the steel sheet to hot-dip galvanizing:

$$0.85 \leq \{[P(wt.\%) + (2/3)] \times 1150\} / \{T\ (°C)\} \leq 1.15 \qquad (2)$$

$$0.35 \leq \{[P(wt.\%) + (2/3)] \times (-30)\} / \{t\ (°C)\} \leq 1.8 \qquad (3)$$

(23) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating

adhesion according to any one of (11) to (22) above, wherein the slab further contains one or more selected from the group consisting of up to 1.0 wt.% Nb, up to 1.0 wt.% Ti and up to 1.0 wt.% V.

(24) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to any one of (11) to (22) above, wherein the slab further contains one or more selected from the group consisting of from 0.001 to 1.0 wt.% Nb, from 0.001 to 1.0 wt.% Ti, and from 0.001 to 1.0 wt.% V.

(25) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to any one of (11) to (24) above, wherein the coating weight of the high strength hot-dip galvanized steel sheet, as represented by the coating weight per side of the steel sheet, of from 20 to 120 g/m^2.

(26) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to any one of (13), (14), (17), (18), (21) and (22) above, wherein, when the hydrogen concentration of the atmosphere gas is within a range of from 1 vol.% to under 100 vol.%, the remaining gas is an inert gas.

(27) A manufacturing method of a high strength hot-dip galvanized steel sheet excellent in workability and coating adhesion according to (26) above, wherein the inert gas is nitrogen gas.

(28) A manufacturing method of a high strength galvannealed steel sheet excellent in workability and coating adhesion, comprising the step of subjecting the hot-dip galvanized steel sheet obtained by the manufacturing method of a high strength hot-dip galvanized steel sheet according to any one of (11) to (27) above further to a galvannealing treatment.

(29) A manufacturing method of a high strength galvannealed steel sheet excellent in workability and coating adhesion, comprising the steps of subjecting the hot-dip galvanized steel sheet according to any one of (11) to (27) above further to a galvannealing treatment, wherein the temperature: t_2 (°C) in the galvannealing treatment satisfies the following equation (4) relative to the P content in steel: P (wt.%) and the Al content: Al (wt.%) in the bath upon the hot-dip galvanizing:

$$0.95 \leq [7 \times \{ 100 \times [P(wt.\%)+(2/3)] + 10 \times Al(wt.\%) \}] / [t_2 (°C)] \leq 1.05 \quad (4)$$

(30) A manufacturing method of a high strength galvannealed steel sheet excellent in workability and coating adhesion according to (28) or (29) above, wherein the slab further contains one or more selected from the group consisting of up to 1.0 wt.% Nb, up to 1.0 wt.% Ti and up to 1.0 wt.% V.

(31) A manufacturing method of a high strength galvannealed steel sheet excellent in workability and coating adhesion according to (28) or (29) above, wherein the slab further contains one or more selected from the group consisting of from 0.001 to 1.0 wt.% Nb, from 0.001 to 1.0 wt.% Ti and from 0.001 to 1.0 wt.% V.

(32) A manufacturing method of a high strength galvannealed steel sheet excellent in workability and coating adhesion according to any one of (28) to (31) above, wherein the coating weight of the galvannealing layer of the high strength galvannealed steel sheet is within a range of from 20 to 120 g/ m^2 as represented by the coating weight per side of the steel sheet.

(33) A high strength galvannealed steel sheet excellent in workability, coating adhesion and corrosion resistance, obtained by hot-dip galvanizing a steel sheet containing up to 1.00 wt.% Mo and then subjecting the steel sheet to galvannealing, wherein, in the galvannealing layer, the Fe content is within a range of from 8 to 11 wt.%, and the Mo content is within a range of from 0.002 to 0.11 wt.%.

(34) A high strength galvannealed steel sheet excellent in workability, coating adhesion and corrosion resistance, obtained by hot-dip galvanizing a steel sheet containing up to 1.00 wt.% Mo and from 0.010 to 0.2 wt.% C and then subjecting the steel sheet to galvannealing, wherein, in the galvannealing layer, the Fe content is within a range of from 8 to 11 wt.%, and the Mo content is within a range of from 0.002 to 0.11 wt.%.

(35) A high strength galvannealed steel sheet excellent in workability, coating adhesion and corrosion resistance according to (33) or (34) above, wherein the steel sheet containing up to 1.00 wt.% Mo contains Mo in an amount within a range of from 0.01 to 1.00 wt.%, ore preferably, from 0.05 to 1.00 wt.%.

(36) A high strength galvannealed steel sheet excellent in workability coating adhesion and corrosion resistance according to any one of (33) to (35) above, wherein the substrate steel sheet serving as the steel sheet is a steel sheet comprising a chemical composition further containing up to 1.0 wt.% Si, from 1.0 to 3.0 wt.% Mn, up to 0.10 wt.% P, up to 0.05 wt.% S, up to 0.10 wt.% Al, up to 0.010 wt.% N, up to 1.0 wt.% Cr and the balance Fe and incidental impurities.

(37) A high strength galvannealed steel sheet excellent in workability, coating adhesion and corrosion resistance according to any one of (33) to (36), wherein the substrate steel sheet serving as the steel sheet further contains one or more selected from the group consisting of up to 1.0 wt.% Nb, up to 1.0 wt.% Ti and up to 1.0 wt.% V.

(38) A high strength galvannealed steel sheet excellent in workability coating adhesion and corrosion resistance according to any one of (33) to (36) above, wherein the substrate steel sheet serving as the steel sheet further contains one or more selected from the group consisting of from 0.001 to 1.0 wt.% Nb, from 0.001 to 1.0 wt% Ti and from 0.001 to 1.0 wt.% V.

(39) A high strength galvannealed steel sheet excellent workability, coating adhesion and corrosion resistance according to any one of (33) to (38) above, wherein the coating weight of the galvannealing layer of the high strength galvannealed steel sheet is within a range of from 20 to 120 g/m^2 as represented by a coating weight per side of the steel.

Brief Description of Drawings

[0033]

Fig. 1 is a graph illustrating the relationship between tensile strength (TS), yield ratio (YR) and TS × El value of a steel sheet, on the one hand, and the [average thickness of band-shaped secondary phase T_b /thickness T], on the other hand;

Fig. 2 illustrates a microphotograph (a) of a metal structure showing a typical band-shaped secondary phase structure and a schematic view (b) of the metal structure;

Fig. 3 illustrates a microphotograph (a) of a metal structure showing a state in which the secondary phase structure dispersed by the first run of heating, and a schematic view (b) of the metal structure;

Fig. 4 is a graph illustrating the relationship between the P content in steel and the optimum heating-reduction temperature region within which non-galvanized defects do not occur;

Fig. 5 is a graph illustrating the optimum regions for the hydrogen concentration and dew point of the atmosphere gas during heating-reduction in which non-galvanized defects do not occur;

Fig. 6 is a graph illustrating the relationship between the P content in steel and the optimum galvannealing temperature region giving a satisfactory coating adhesion;

Fig. 7 is a graph illustrating the relationship between the Mo content in the galvanizing layer and the weight loss by corrosion;

Fig. 8 is a graph illustrating the relationship between the P content in steel and the optimum heating-reduction temperature region within which non-galvanized defects do not occur; and

Fig. 9 is a graph illustrating the relationship between the P content in steel and the optimum region of dew point of the atmosphere gas during heating-reduction in which non-galvanized defect do not occur.

Best Mode for Carrying Out the Invention

[0034] First, the result of experiment carried out to improve mechanical properties and forming the basis for the present invention will be described.

[0035] A sheet bar having a chemical composition comprising 0.09 wt.% C, 0.01 wt.% Si, 2.0 wt.% Mn, 0.009 wt.% P, 0.003 wt.% S, 0.041 wt.% Al, 0.0026 wt.% N, 0.15 wt.% Mo, 0.02 wt.% Cr, and the balance substantially Fe, and having a thickness of 30 mm was heated to 1,200 °C, rolled into a hot-rolled steel sheet having a thickness of 2.5 mm through five passes. The hot-rolled steel sheet was coiled at 640°C, pickled, heating and held at a temperature within a range of from 750 to 900°C for a minute (first run of heating), and then, cooled to the room temperature at a cooling rate of 10°C /s.

To control band structure.

[0036] Then, the steel sheet was heated and held at 750°C for a minute (second run of heating), cooled to 500°C at a cooling rate of 10°C/s, held for 30 seconds, heated to 550°C at a heating rate of 10°C/s, and immediately holding for 20 seconds, cooled to the room temperature at a cooling rate of 10°C/s.

[0037] For the resultant steel sheet, the relationship between TS, YR and TS × El value, on the one hand, and the band structure thickness on the thickness direction in cross-section of the steel sheet after the first run of heating, on the other hand, was investigated. The result is shown in Fig. 1.

[0038] The band structure thickness is expressed by T_b / T (where, T_b: thickness of the band structure in the thickness direction comprising a secondary phase, T: steel sheet thickness).

[0039] T_b is an average over values obtained by measurement of all the band structures in the thickness direction in a image of 1,500 magnification by means of an image analyzer.

[0040] Fig. 1 reveals that a T_b / T of up to 0.005 in the steel sheet after the first run of heating leads to a low yield ratio and a satisfactory TS × El value.

[0041] More specifically, when Mn is added in a large quantity for the purpose of ensuring a high strength as in the present invention, a band structure rich in C and Mn, comprising mainly the secondary phase composed of cementite, pearlite and bainite tends to easily grow.

[0042] In such a case, it is possible to simultaneously achieve a good workability and a high tensile strength by carrying out the first run of heating at a prescribed temperature on a facility such as a continuous annealing line, prior to conducting heating on a continuous hot-dip galvanizing line (CGL) (second run of heating), which reduces the band structure thickness, through fine dispersion of band structures. Even when the band structures are dissolved during

heating on the continuous hot-dip galvanizing line and held in the galvanizing process or even during galvannealing treatment, martensite grains are appropriately dispersed in the ferrite substrate.

[0043] This is a phenomenon which may take place when the steel sheet is heated at a high temperature on the continuous hot-dip galvanizing line. Even with a single run of heating on the continuous hot-dip galvanizing line, there is no charge in material quality.

[0044] However, a high-temperature heating may cause deterioration of galvanizability because of the tendency of Mn concentrated on the steel sheet surface. In order to achieve a more stable galvanizability, therefore, it is desirable to conduct a first run of heating on the continuous annealing line, and more preferably, to carry out a second run of heating on the continuous hot-dip galvanizing line.

[0045] This dispersion effect of the band structures brought about by the first run of heating is evident from the comparison of microphotographs illustrated in Figs. 2 and 3.

[0046] Fig. 2(a) illustrates a metal structure before the first run of heating, and Fig. 2(b) is a schematic view of Fig. 2(a).

[0047] Fig. 3(a) illustrates a metal structure after the first run of heating, and Fig. 3(b) is a schematic view of Fig. 3(a).

[0048] In Figs. 2(b) and 3(b), B.S. represents band structures comprising a secondary phase mainly consisting of cementite, pearlite, bainite, and very partially martensite and residual austenite.

[0049] In the structure before the first run of heating shown in Fig. 2, T_b / T takes a value of 0.0070 on the average. In the structure after the first run of heating shown in Fig. 3, in contrast, dispersion of band structures is attempted, and the value of T_b /T decreases to 0.0016 on the average.

[0050] The present invention for further improving galvanizability will now be described in detail.

[0051] As a result of studies on the composition of the substrate steel sheet annealing conditions and galvannealing conditions necessary for preventing non-galvanized defects and improving workability and coating adhesion, the present inventors obtained the following findings (1) to (3) and developed the present invention.

(1) Two-stage heating-pickling process

[0052] A high strength hot-dip galvanized steel sheet permitting prevention of non-galvanized defects and excellent in coating adhesion and corrosion resistance is available by heating a steel sheet having a prescribed chemical composition to a temperature of at least 750°C, or preferably, at least 800°C in an annealing furnace, cooling the same, pickling the steel sheet to remove a concentrated layer of steel constituents on the steel sheet surface, then annealing again the steel sheet on a continuous hot-dip galvanizing line in a prescribed reducing atmosphere at an appropriate heating-reduction temperature and then subjecting the steel sheet to hot-dip galvanizing.

[0053] The aforementioned method of treatment prior to hot-dip galvanizing (:heating in annealing furnace → pickling → heating-reduction) is hereinafter called the two-stage heating-pickling process.

(2) Single-stage heating process

[0054] As a result of further studies, availability was found of satisfactory galvanizability and coating adhesion by single-stage heating by heating a steel sheet having a prescribed chemical composition at an appropriate heating temperature in a hydrogen-containing gas having an appropriate dew point, and then subjecting the steel sheet to hot-dip galvanizing.

[0055] The aforementioned heating method prior to hot-dip galvanizing (;heating-reduction) will hereinafter be called also the single-stage heating process.

(3) Galvannealing process

[0056] Availability was found of a high strength galvannealed steel sheet excellent both in coating adhesion and corrosion resistance after galvannealing by annealing the hot-dip galvanized steel sheet obtained in (1) and (2) above preferably under conditions satisfying a prescribed galvannealing temperature requirement.

[0057] Experiments forming the basis for the present invention for improving the aforementioned galvanizability will now be described.

[Two-stage heating-pickling process]

[0058] A sheet bar having a chemical composition comprising 0.09 wt.% C, 0.01 wt.% Si, 2.0 wt.% Mn, from 0.005 to 0.1 wt.% P, 0.003 wt.% S, 0.041 wt.% Al, 0.0026 wt.% N, 0.15 wt.% Mo, 0.02 wt.% Cr and the balance substantially Fe, and having a thickness of 30 mm was heated to 1,200°C, and rolled into a hot-rolled steel sheet having a thickness

of 2.5 mm through five passes.

[0059] The resultant hot-rolled steel sheet was treated in the sequence of the following (1) to (10):

(1): heat treat at 540°C for 30 minutes, and subjected to a treatment corresponding to coiling;
(2): pickled for 40 seconds in a 5 wt.% HCl solution having a liquid temperature of 80 °C;
(3): held at 800°C (steel sheet temperature) for a minute in a reducing atmosphere containing hydrogen in an annealing furnace;
(4): cooled to the room temperature at a cooling rate of 10°C/s;
(5): pickled for 10 seconds in a 5 wt.% HCl solution having a liquid temperature of 60°C;
(6): held for 20 seconds at 650 to 950°C (steel sheet temperature) in a reducing atmosphere containing hydrogen;
(7): cooled to 480°C at a cooling rate of 10°C/s;
(8): subjected to hot-dip galvanizing by dipping for a second into a hot-dip galvanizing bath containing 0.15 wt.% Al and having a bath temperature of 480°C;
(9): the coating weight of the galvanized steel sheet pulled up from the hot-dip galvanizing bath is objected to 50 g/m^2 through gas wiping;
(10): immediately after heating-reduction under conditions including an H_2 concentration of 7 vol.%, a dew point (:dp) of - 25°C and a steel sheet temperature of 800°C, subjected to hot-dip galvanizing under the above-mentioned conditions, and the resultant hot-dip galvanized steel sheet is subjected to a galvannealing treatment at 450 to 600°C.

[0060] Then, properties of the resultant steel sheet were evaluated with the following method of evaluation and criteria.

[Galvanizability]

[0061] The exterior view of the hot-dip galvanized steel sheet (hot-dip galvanized steel sheet not as yet galvannealed) was visually inspected.

○: Non-galvanized defects completely non-existent (good galvanizability);
X: Non-galvanized defects occurred.

[Coating adhesion]

[0062] The galvanized steel sheet was bent to 90° and straightened, then the galvanizing layer on the compressed side was peeled off with a cellophane tape, and evaluation was made on the basis of the amount of galvanizing film adhering to the cellophane tape.

(Galvanized steel sheet not as yet galvannealed)

[0063]

○ : No peeling of the galvanizing layer (good coating adhesion)
X: The galvanizing layer was peeled off (defective coating adhesion

(Galvannealed steel sheet)

[0064]

○ : Small amount of peeled galvanizing layer (good coating adhesion)
X: Large amount of peeled galvanizing layer (poor coating adhesion)

[Exterior view after galvannealing]

[0065] The exterior view after galvannealing was visually evaluated.

○ : Uniform exterior view without unevenness of galvannealing
X: Unevenness of galvannealing occurs